

^b Beijing Key Laboratory for Sensor, School of Science, Beijing Information Science and Technology University, Beijing 100101, China

^c Key Laboratory of the Ministry of Education for Optoelectronic Measurement Technology and Instrument, Beijing Information Science and Technology University, Beijing 100192, China

* Correspondence: li@bistu.edu.cn;

Improved Perovskite Crystallization by Antisolvent Engineering in Tin-Perovskite Photovoltaics

Xin Zhang,^{ab} Yu Liu,^{ab} Xinyao Chen,^a Chunqian Zhang,^b Jigang Wang,^c Jin Cheng^b and Junming Li^{*b}

^a Key Laboratory of Modern Measurement & Control Technology, Ministry of Education, Beijing Information Science and Technology University, Beijing 100192, China

^b Beijing Key Laboratory for Sensor, School of Science, Beijing Information Science and Technology University, Beijing 100101, China

^c Key Laboratory of the Ministry of Education for Optoelectronic Measurement Technology and Instrument, Beijing Information Science and Technology University, Beijing 100192, China

* Correspondence: li@bistu.edu.cn;

Table S1. Statistics of photovoltaic performance parameters of tin-based perovskite solar cells.

Year	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Ref
2014	0.88	16.8	42	6.4	1
2014	0.82	12.3	57	5.7	2
2016	0.47	22.07	60.67	6.22	3
2017	0.61	21.2	62.7	8.12	4
2017	0.53	24.1	71	9	5
2018	0.62	21.2	72.9	9.6	6
2020	0.84	20.32	78	13.24	7
2021	0.84	24.91	70.76	14.81	8
2022	0.77	24.9	76.7	14.7	9
2022	0.92	20.4	76.7	14.3	10
2023	0.91	20.6	78.6	14.6	11
2024	0.86	24.81	72.37	15.4	12
2024	0.97	21.7	74.1	15.7	13

Table S2. Fundamental physical parameters of DMF, DMSO, CB, DMS.

Solvents	Donor number (kcal/mol)	Dielectric constant	Dipole moment (D)	Boiling point (°C)	Vapor pressure at 20 °C (kPa)
DMF	26.6	36.7	3.7	153	0.38
DMSO	29.8	46.6	4.1	189	0.05
CB	3.3	5.6	1.5	132	1.17
DMS	40.0	6.3	1.5	38	53.7

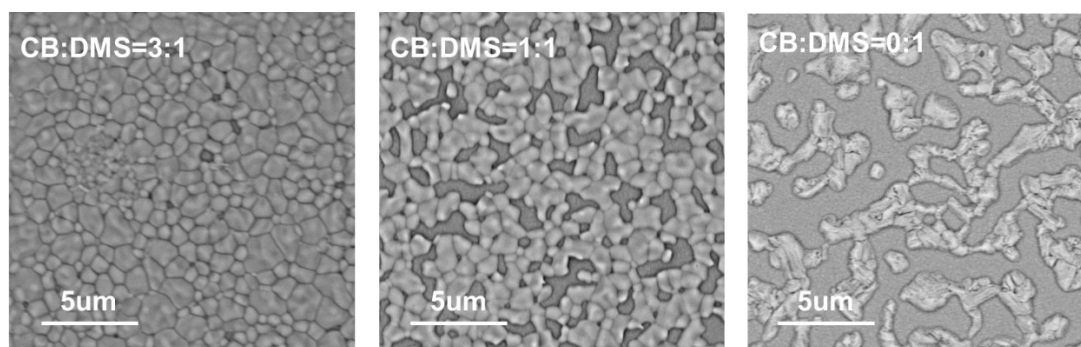


Fig. S1 Top-view scanning electron microscopy images of different ratios of CB and DMS.

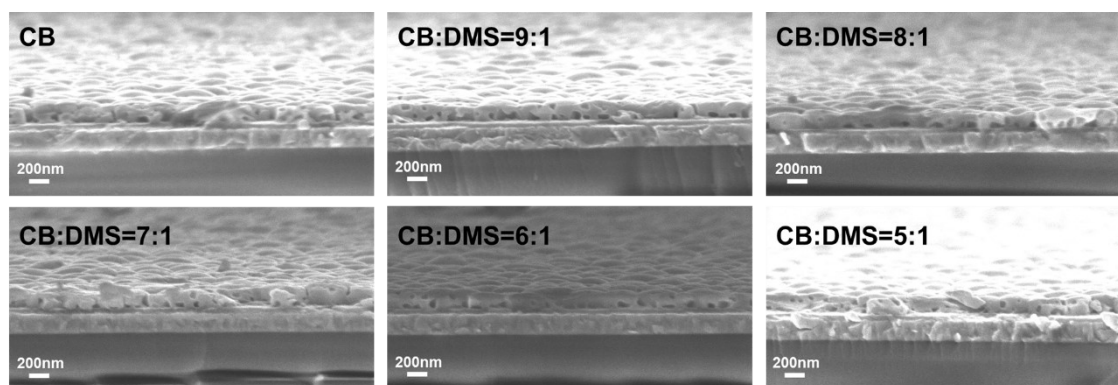


Fig. S2 Cross-sectional SEM images of tin-based perovskite films based on different antisolvent ratios.

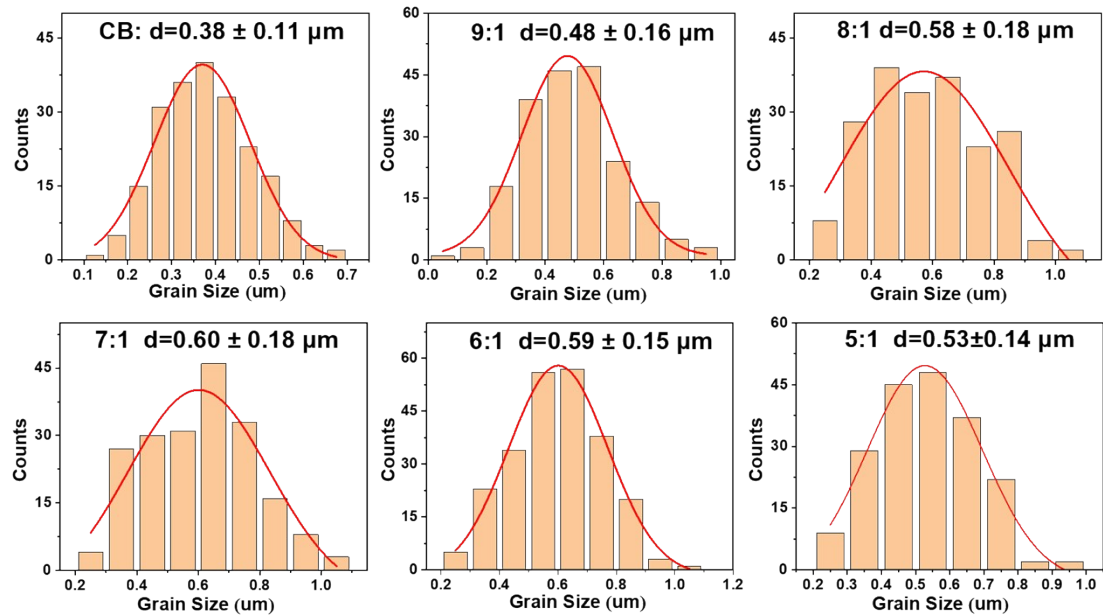


Fig. S3 Grain diameter distribution of tin-based perovskite films with different antisolvent ratios.

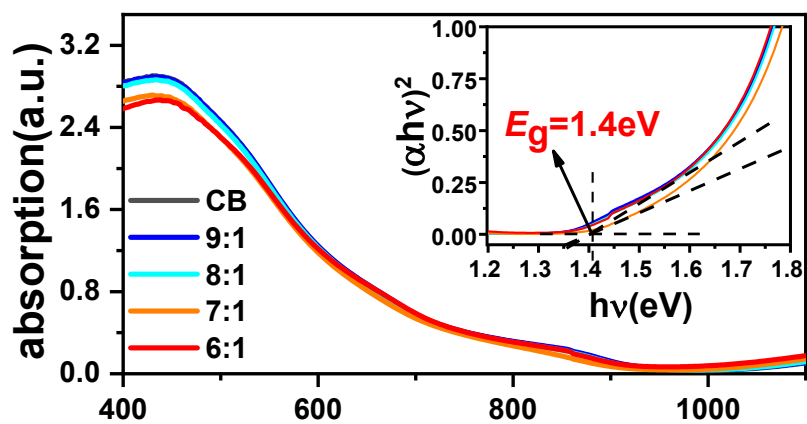


Fig. S4 UV-vis absorption spectrum of perovskite films with different proportions of antisolvent. Inset shows the Tauc plot.

Table S3. Percentage of XPS peak area of Sn⁴⁺ and Sn²⁺ for tin-based PSCs with different antisolvent ratios.

CB:DMS	Sn 3d5/2		Sn 3d3/2	
	Sn ²⁺	Sn ⁴⁺	Sn ²⁺	Sn ⁴⁺
CB	31.90 %	17.94 %	32.11 %	18.05 %
9:1	33.02 %	16.82 %	33.23 %	16.93 %
8:1	34.47 %	15.37 %	34.69 %	15.47 %
7:1	35.43 %	14.41 %	35.65 %	14.51 %
6:1	37.00 %	12.84 %	37.24 %	12.92 %
5:1	33.60 %	16.32 %	33.80 %	16.27 %

Table S4. Photovoltaic performance parameters of tin-based perovskite solar cells with different antisolvent ratios.

CB: DMS	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)	PCE (%)
1:0	0.39	18.3	58.30	4.2
9:1	0.42	18.0	59.28	4.5
8:1	0.41	20.1	55.79	4.2
7:1	0.44	18.0	61.79	4.9
6:1	0.44	19.8	64.19	5.3
5:1	0.45	14.7	63.92	4.3

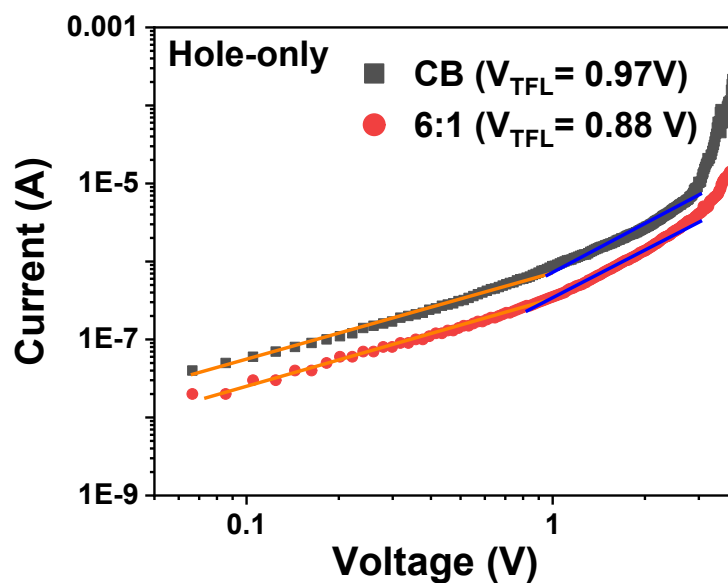


Fig. S5 SCLC curve of hole-only devices prepared with CB and CB:DMS=6:1 as anti-solvent.

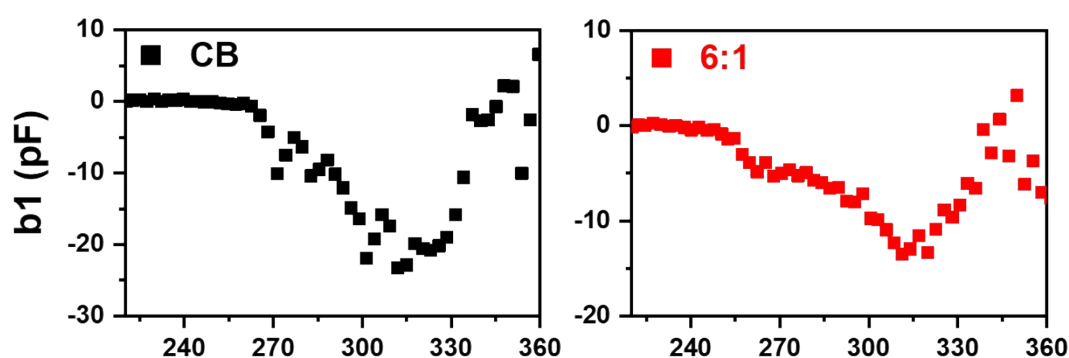


Fig. S6 Deep-level transient spectroscopy (DLTS) signal from CB device (black) and CB:DMS=6:1 device (red).

References :

- Noel, N. K.; Stranks, S. D.; Abate, A.; Wehrenfennig, C.; Guarnera, S.; Haghighirad, A.-A.; Sadhanala, A.; Eperon, G. E.; Pathak, S. K.; Johnston, M. B.; Petrozza, A.; Herz, L. M.; Snaith, H. J., Lead-free organic-inorganic tin halide perovskites for photovoltaic applications. *Energy Environ. Sci.* **2014**, 7 (9), 3061-3068.
- Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G., Lead-free solid-state organic-inorganic halide perovskite solar cells. *Nature Photonics* **2014**, 8 (6), 489-494.
- Liao, W.; Zhao, D.; Yu, Y.; Grice, C. R.; Wang, C.; Cimaroli, A. J.; Schulz, P.; Meng, W.; Zhu, K.; Xiong, R. G.; Yan, Y., Lead-Free Inverted Planar Formamidinium Tin Triiodide Perovskite Solar Cells Achieving Power Conversion Efficiencies up to 6.22. *Adv Mater* **2016**, 28 (42), 9333-9340.
- Zhao, Z.; Gu, F.; Li, Y.; Sun, W.; Ye, S.; Rao, H.; Liu, Z.; Bian, Z.; Huang, C., Mixed-Organic-Cation Tin Iodide for Lead-Free Perovskite Solar Cells with an Efficiency of 8.12. *Adv Sci (Weinh)* **2017**, 4 (11), 1700204.
- Shao, S.; Liu, J.; Portale, G.; Fang, H. H.; Blake, G. R.; ten Brink, G. H.; Koster, L. J. A.; Loi,

- M. A., Highly Reproducible Sn-Based Hybrid Perovskite Solar Cells with 9% Efficiency. *Advanced Energy Materials* **2017**, *8* (4).
6. Jokar, E.; Chien, C. H.; Tsai, C. M.; Fathi, A.; Diau, E. W., Robust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10. *Adv Mater* **2019**, *31* (2), e1804835.
 7. Nishimura, K.; Kamarudin, M. A.; Hirotsu, D.; Hamada, K.; Shen, Q.; Iikubo, S.; Minemoto, T.; Yoshino, K.; Hayase, S., Lead-free tin-halide perovskite solar cells with 13% efficiency. *Nano Energy* **2020**, *74*.
 8. Yu, B. B.; Chen, Z.; Zhu, Y.; Wang, Y.; Han, B.; Chen, G.; Zhang, X.; Du, Z.; He, Z., Heterogeneous 2D/3D Tin-Halides Perovskite Solar Cells with Certified Conversion Efficiency Breaking 14. *Adv Mater* **2021**, *33* (36), e2102055.
 9. Zhou, J.; Hao, M.; Zhang, Y.; Ma, X.; Dong, J.; Lu, F.; Wang, J.; Wang, N.; Zhou, Y., Chemo-thermal surface dedoping for high-performance tin perovskite solar cells. *Matter* **2022**, *5* (2), 683-693.
 10. Zhu, Z.; Jiang, X.; Yu, D.; Yu, N.; Ning, Z.; Mi, Q., Smooth and Compact FASnI₃ Films for Lead-Free Perovskite Solar Cells with over 14% Efficiency. *ACS Energy Letters* **2022**, *7* (6), 2079-2083.
 11. Li, H.; Zang, Z.; Wei, Q.; Jiang, X.; Ma, M.; Xing, Z.; Wang, J.; Yu, D.; Wang, F.; Zhou, W.; Wong, K. S.; Chow, P. C. Y.; Zhou, Y.; Ning, Z., High-member low-dimensional Sn-based perovskite solar cells. *Science China Chemistry* **2023**, *66* (2), 459-465.
 12. Chen, J.; Luo, J.; Hou, E.; Song, P.; Li, Y.; Sun, C.; Feng, W.; Cheng, S.; Zhang, H.; Xie, L.; Tian, C.; Wei, Z., Efficient tin-based perovskite solar cells with trans-isomeric fulleropyrrolidine additives. *Nature Photonics* **2024**, *18* (5), 464-470.
 13. Shi, Y.; Zhu, Z.; Miao, D.; Ding, Y.; Mi, Q., Interfacial Dipoles Boost Open-Circuit Voltage of Tin Halide Perovskite Solar Cells. *ACS Energy Letters* **2024**, *9* (4), 1895-1897.